Comparison of Excessive Balmer α Line Broadening of Glow Discharge and Microwave Hydrogen Plasmas with Certain Catalysts

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ABSTRACT

From the width of the 656.2 nm Balmer α line emitted from microwave and glow discharge plasmas, it was found that a strontium-hydrogen microwave plasma showed a broadening similar to that observed in the glow discharge cell of 27 - 33 eV; whereas, in both sources, no broadening was observed for magnesium-hydrogen. Microwave helium-hydrogen and argon-hydrogen plasmas showed extraordinary broadening corresponding to an average hydrogen atom temperature of 110 - 130 eV and 180 - 210 eV, respectively. The corresponding results from the glow discharge plasmas were 30 - 35 eV and 33 - 38 eV, respectively, compared to ≈ 4 eV for plasmas of pure hydrogen, neon-hydrogen, krypton-hydrogen, and xenon-hydrogen maintained in either source. Similarly, the average electron temperature T_e for helium-hydrogen and argon-hydrogen microwave plasmas were high, $28{,}000 \pm 5\%$ K and $11{,}600 \pm 5\%$ K, respectively; compared to $6800 \pm 5\%$ K and $4800 \pm 5\%$ K for helium and argon alone, respectively. Stark broadening or acceleration of charged species due to high fields can not explain the microwave results since no high field was present. Rather, a resonant energy transfer mechanism is proposed.

Key Words: microwave plasma, glow discharge plasma, significant line broadening, electron temperature, resonant energy transfer mechanism

I. INTRODUCTION

Glow discharge devices have been developed over decades as light sources, ionization sources for mass spectroscopy, excitation sources for optical spectroscopy, and sources of ions for surface etching and chemistry [1-3]. A Grimm-type glow discharge is a well established excitation source for the analysis of conducting solid samples by optical emission spectroscopy [4-6]. Despite extensive performance characterizations, data was lacking on the plasma parameters of these devices. M. Kuraica and N. Konjevic [7] and Videnocic et al. [8] have characterized these plasmas by determining the excited hydrogen atom concentrations and energies from measurements of the line broadening of the 656.2 nm Balmer α line. The data was analyzed in terms of Stark and Doppler effects wherein acceleration of charges such as H^+, H_2^+, and H_3^+ in the high fields (e. g. over $10\,kV/cm$) which were present in the cathode fall region was used to explain the Doppler component.

More recently, microhollow glow discharges have been spectroscopically studied as candidates for the development of an intense monochromatic EUV light source (e.g. Lyman α) for short wavelength lithograph for production of the next generation of integrated circuits. A neon-hydrogen microhollow cathode glow discharge has been proposed as a source of predominantly Lyman α radiation. Kurunczi, Shah, and Becker [9] observed intense emission of Lyman α and Lyman β radiation at 121.6 nm and 102.5 nm, respectively, from microhollow cathode discharges in high-pressure Ne (740 Torr) with the addition of a small amount of hydrogen (up to 3 Torr). With essentially no molecular emission observed, Kurunczi et al. attributed the anomalous Lyman α emission to the near-resonant energy transfer between the Ne_2^* excimer and H_2 which leads to formation of $H(n=2)$ atoms, and attributed the Lyman β emission to the near-resonant energy transfer between excited Ne^* atoms (or vibrationally excited neon excimer molecules) and H_2 which leads to formation of $H(n=3)$ atoms. Despite the emission characterization of this source, data is lacking about plasma parameters.

For analyses of solids, direct current (dc) glow discharge sources have been successfully complemented by radio-frequency (rf) discharges [10]. The use of dc discharges is limited to metals; whereas, rf discharges

are applicable to non-conducting materials. Other developed sources that provide a usefully intense plasma are synchrotron devices, inductively coupled plasma generators [11], and magnetically confined plasmas. Plasma characterization data on these sources is also limited.

A new plasma source has been developed that operates by incandescently heating a hydrogen dissociator and a catalyst to provide atomic hydrogen and gaseous catalyst, respectively, such that the catalyst reacts with the atomic hydrogen to produce a plasma. It was extraordinary, that intense EUV emission was observed by Mills et al. [12-19] at low temperatures (e.g. $\approx 10^3\,K$) from atomic hydrogen and certain atomized elements or certain gaseous ions which singly or multiply ionize at integer multiples of the potential energy of atomic hydrogen, $27.2\,eV$ that comprise catalysts. The only pure elements that were observed to emit EUV were those wherein the ionization of t electrons from an atom to a continuum energy level is such that the sum of the ionization energies of the t electrons is approximately $m \cdot 27.2\,eV$ where t and m are each an integer.

Since Ar^+, He^+, and strontium each ionize at an integer multiple of the potential energy of atomic hydrogen, a discharge with one or more of these species present with hydrogen is anticipated to form a plasma called a resonance transfer (rt) plasma. The plasma forms by a resonance transfer mechanism involving the species providing a net enthalpy of a multiple of $27.2\,eV$ and atomic hydrogen.

Mills and Nansteel [14, 19] have reported that strontium atoms each ionize at an integer multiple of the potential energy of atomic hydrogen and caused emission. (The enthalpy of ionization of Sr to Sr^{5+} has a net enthalpy of reaction of $188.2\,eV$, which is equivalent to $m=7$.) The emission intensity of the plasma generated by atomic strontium increased significantly with the introduction of argon gas only when Ar^+ emission was observed. Whereas, no emission was observed when chemically similar atoms that do not ionize at integer multiples of the potential energy of atomic hydrogen (sodium, magnesium, or barium) replaced strontium with hydrogen, hydrogen-argon mixtures, or strontium alone.

Mills and Nanstell [14, 19] measured the power balance of a gas cell having vaporized strontium and atomized hydrogen from pure hydrogen

or argon-hydrogen mixture (77/23%) by integrating the total light output corrected for spectrometer system response and energy over the visible range. Hydrogen control cell experiments were identical except that sodium, magnesium, or barium replaced strontium. In the case of hydrogen-sodium, hydrogen-magnesium, and hydrogen-barium mixtures, 4000, 7000, and 6500 times the power of the hydrogen-strontium mixture was required, respectively, in order to achieve that same optically measured light output power. With the addition of argon to the hydrogen-strontium plasma, the power required to achieve that same optically measured light output power was reduced by a factor of about two. The power required to maintain a plasma of equivalent optical brightness with strontium atoms present was 8600 and 6300 times less than that required for argon-hydrogen and argon control, respectively. A plasma formed at a cell voltage of about 250 V for hydrogen alone and sodium-hydrogen mixtures, 140-150 V for hydrogen-magnesium and hydrogen-barium mixtures, 224 V for an argon-hydrogen mixture, and 190 V for argon alone; whereas, a plasma formed for hydrogen-strontium mixtures and argon-hydrogen-strontium mixtures at extremely low voltages of about 2 V and 6.6 V, respectively.

It was reported [13] that characteristic emission was observed from a continuum state of Ar^{2+} which confirmed the resonant nonradiative energy transfer of $27.2\,eV$ from atomic hydrogen Ar^{+}. The transfer of $27.2\,eV$ from atomic hydrogen to Ar^{+} in the presence of a electric weak field resulted in its excitation to a continuum state. Then, the energy for the transition from essentially the Ar^{2+} state to the lowest state of Ar^{+} was predicted to give a broad continuum radiation in the region of $45.6\,nm$. This broad continuum emission was observed. This emission was dramatically different from that given by an argon microwave plasma wherein the entire Rydberg series of lines of Ar^{+} was observed with a discontinuity of the series at the limit of the ionization energy of Ar^{+} to Ar^{2+}. The observed Ar^{+} continuum in the region of $45.6\,nm$ confirmed the rt-plasma mechanism of the excessively bright, extraordinarily low voltage discharge. With Ar^{+} as the catalyst, the product hydride ion was predicted to have a binding energy of $3.05\,eV$, and it was observed spectroscopically at $407\,nm$ [13].

He^{+} ionizes at $54.417\,eV$ which is $2 \cdot 27.2\,eV$, and novel EUV emission

lines were observed from microwave and glow discharges of helium with 2% hydrogen [20]. The observed energies were $q \cdot 13.6\ eV$ ($q = 1,2,3,4,6,7,8,9,$ *or* 11) or these energies less $21.2\ eV$ due to inelastic scattering of the lines by helium atoms in the excitation of $He(1s^2)$ to $He(1s^1 2p^1)$. These lines can be explained by the resonance transfer of $m \cdot 27.2\ eV$ [20].

It was anticipated that microwave and glow discharges would also provide atomic hydrogen and vaporized catalyst to form a rt-plasma. To further characterize the plasma parameters observed in rt-plasmas and to study the difference between microwave and discharge sources, 1.) a comparison between the width of the Lyman α line of an argon-hydrogen plasma emitted from a glow discharge cell and a microwave cell was compared, 2.) by measuring the line broadening of the 656.2 nm Balmer α line, the excited hydrogen atom energy and concentration were determined on plasmas of hydrogen and a catalyst or plasmas comprising hydrogen with chemically similar controls that did not provide gaseous ions having electron ionization energies which are a multiple of $27.2\ eV$, and 3.) the electron temperature T_e was measured on microwave plasmas using the ratio of the intensity I of two noble gas or metal lines in two quantum states such as the ratio $I(He\ 501.6\ nm\ line)/\ I(He\ 492.2\ nm\ line)$ and the ratio $I(Ar\ 104.8\ nm\ line)/\ I(Ar\ 420.06\ nm\ line)$ for plasmas having helium and argon, respectively, alone or as a mixture with hydrogen.

II. EXPERIMENTAL

A. Measurement of Lyman α emission by EUV spectroscopy

Extreme ultraviolet (EUV) spectroscopy was recorded on microwave and discharge cell light sources. Due to the extremely short wavelength of this radiation, "transparent" optics do not exist. Therefore, a windowless arrangement was used wherein the microwave or discharge cell was connected to the same vacuum vessel as the grating and detectors of the extreme ultraviolet (EUV) spectrometer. Differential pumping permitted a high pressure in the cell as compared to that in the spectrometer. This was achieved by pumping on the cell outlet and pumping on the grating side of the collimator that served as a pin-hole

inlet to the optics. The spectrometer was continuously evacuated to $10^{-4}-10^{-6}$ torr by a turbomolecular pump with the pressure read by a cold cathode pressure gauge. The EUV spectrometer was connected to the cell light source with a 1.5 mm X 5 mm collimator which provided a light path to the slits of the EUV spectrometer. The collimator also served as a flow constrictor of gas from the cell. The cell was operated under gas flow conditions while maintaining a constant gas pressure in the cell.

Spectra were obtained on glow discharge and microwave plasmas of an argon-hydrogen mixture (97/3%). Each gas was ultrahigh pure. The gas pressure inside the cell was maintained at about 300 mtorr with an argon flow rate of 5.2 sccm and a hydrogen flow rate of 0.3 sccm. Each gas flow was controlled by a 0-20 sccm range mass flow controller (MKS 1179A21CS1BB) with a readout (MKS type 246).

For spectral measurement, the light emission from discharge and microwave plasmas of argon-hydrogen (97/3%) was introduced to a normal incidence McPherson 0.2 meter monochromator (Model 302, Seya-Namioka type) equipped with a 1200 lines/mm holographic grating with a platinum coating. The wavelength region covered by the monochromator was $5-560\,nm$. The UV spectrum ($100-170\,nm$) of the cell emission was recorded with a photomultiplier tube (PMT) and a sodium salicylate scintillator. The PMT (Model R1527P, Hamamatsu) used has a spectral response in the range of $185-680\,nm$ with a peak efficiency at about $400\,nm$. The wavelength resolution was about $1\,nm$ (FWHM) with an entrance and exit slit width of $300\,\mu m$. The increment was $0.1\,nm$ and the dwell time was $500\,ms$.

B. Glow discharge emission spectra

The extreme ultraviolet emission spectrum was obtained on an argon-hydrogen mixture (97/3%) glow discharge plasma. A diagram of the discharge plasma source is given in Figure 1. The experimental setup for the discharge measurements is illustrated in Figure 2. The cell comprised a five-way stainless steel cross that served as the anode with a hollow stainless steel cathode. The hollow cathode was constructed of a stainless steel rod inserted into a steel tube, and this assembly was inserted into an Alumina tube. The gas mixture was flowed through the

five-way cross. An AC power supply (U = 0 - 1 kV, I = 0 - 100 mA) was connected to the hollow cathode to generate a discharge at the hollow cathode inside the discharge cell. The AC voltage and current at the time the EUV spectrum was recorded were 200 V and 40 mA, respectively. A Swagelok adapter at the very end of the steel cross provided a gas inlet and a connection with the pumping system, and the cell was pumped with a mechanical pump. Valves were between the cell and the mechanical pump, the cell and the monochromator, and the monochromator and its turbo pump. A flange opposite the end of the hollow cathode connected the spectrometer with the cell. It had a small hole that permitted radiation to pass to the spectrometer. The hollow cathode and EUV spectrograph were aligned on a common optical axis using a laser. The light emission was introduced into a normal incidence EUV spectrometer. (See EUV-Spectroscopy section).

C. Microwave discharge emission spectra

The extreme ultraviolet emission spectrum was obtained on an argon-hydrogen mixture (97/3%) microwave discharge plasma. The experimental set up comprising a microwave discharge gas cell light source and an EUV spectrometer which was differentially pumped is shown in Figure 3. The gas mixture was flowed through a half inch diameter quartz tube fitted with an Opthos coaxial microwave cavity (Evenson cavity). The microwave generator was an Opthos model MPG-4M generator (Frequency: 2450 MHz). The input power to the plasma was set at 40 watts. The light emission was introduced into a normal incidence EUV spectrometer. (See EUV-Spectroscopy section).

D. Measurement of hydrogen ion temperature and number density from Balmer line broadening

The Doppler-broadened line shape for atomic hydrogen has been studied on many sources such as hollow cathode [8, 21] and rf [22-23] discharges. The method of Videnocic et al. [8, 25] was used to calculate the energetic hydrogen atom densities and energies from the width of the 656.2 nm Balmer α line emitted from glow discharge and microwave

plasmas. Gigosos et al. [24] have reviewed the literature and have discussed the limitations of this method. The full half-width $\Delta\lambda_G$ of each Gaussian results from the Doppler ($\Delta\lambda_D$) and instrumental ($\Delta\lambda_I$) half-widths:

$$\Delta\lambda_G = \sqrt{\Delta\lambda_D^2 + \Delta\lambda_I^2} \qquad (1)$$

$\Delta\lambda_I$ in our experiments was $0.006\,nm$. The temperature was calculated from the Doppler half-width using the formula:

$$\Delta\lambda_D = 7.16\,X\,10^{-7}\lambda_0\left(\frac{T}{\mu}\right)^{1/2} \quad (nm) \qquad (2)$$

where λ_0 is the line wavelength in nm, T is the temperature in K ($1\,eV = 11{,}605\,K$), and μ is the molecular weight (=1 for hydrogen). In each case, the average Doppler half-width that was not appreciably changed with pressure varied by ±5% corresponding to an error in the energy of ±5%. The corresponding number densities for noble gas-hydrogen mixtures varied by ±20% depending on the pressure.

a. Balmer line broadening recorded on glow discharge plasmas

The width of the 656.5 nm Balmer α line emitted from gas discharge plasmas having atomized hydrogen from pure hydrogen alone, strontium or magnesium with hydrogen, and a mixture of 10% hydrogen and helium, argon, neon, krypton, or xenon was measured with a high resolution visible spectrometer with a resolution of $\pm 0.025\,nm$ over the spectral range 190-860 nm. The plasmas were maintained in the cylindrical stainless steel gas cell shown in Figure 4.

The 304-stainless steel cell cylindrical cell was 9.21 cm in diameter and 14.5 cm in height. The base of the cell contained a welded-in stainless steel thermocouple well (1 cm OD) which housed a thermocouple probe in the cell interior approximately 2 cm from the discharge and 2 cm from the cell axis. The top end of the cell was welded to a high vacuum 11.75 cm diameter conflat flange. A silver plated copper gasket was placed between a mating flange and the cell flange. The two flanges were clamped together with 10 circumferential bolts. The mating flange contained three penetrations comprising 1.) a stainless steel thermocouple well (1 cm OD) also housing a thermocouple probe in the cell interior approximately 2 cm from the discharge and 2 cm from the

cell axis, 2.) a centered high voltage feedthrough which transmitted the power, supplied through a power connector, to a hollow cathode inside the cell, and 3.) a stainless steel tube (0.95 cm diameter and 100 cm in length) welded flush with the bottom surface of the top flange that served as a vacuum line from the cell and the line to supply the test gas.

The axial hollow cathode glow discharge electrode assembly comprised a stainless steel plate (42 mm diameter, 0.9 mm thick) anode and a circumferential stainless steel cylindrical frame (5.08 cm OD, 7.2 cm long) perforated with evenly spaced 1 cm diameter holes. The cathode was attached to the cell body by a stainless steel wire, and the cell body was grounded.

A 1.6 mm thick UV-grade sapphire window with 1.5 cm view diameter provided a visible light path from inside the cell. The viewing direction was normal to the cell axis.

The cell was sealed in the glove box, removed, and then evacuated with a turbo vacuum pump to a pressure of 4 mTorr. The gas was ultrahigh purity hydrogen or noble gas-hydrogen mixture (90/10%) at 2 Torr total pressure. The pressure of each test gas comprising a mixture with 10% hydrogen was determined by adding the pure noble gas to a given pressure and increasing the pressure with hydrogen gas to a final pressure. The partial pressure of the hydrogen gas was given by the incremental increase in total gas pressure monitored by a 0-10 Torr absolute pressure gauge. The discharge was carried out under static gas conditions. The discharge was started and maintained by a DC electric field supplied by a constant voltage DC power supply at 275 V which produced a current of about 0.2 A. In the case of strontium-hydrogen, helium-hydrogen, and argon-hydrogen plasmas, the voltage was increased at 50 V increments from 275 V to 475 V, and the high resolution visible spectra were recorded to observe the effect of voltage on the Balmer α line broadening.

The plasma emission from the glow discharges of pure hydrogen, strontium or magnesium with hydrogen, and noble gas-hydrogen mixtures was fiber-optically coupled to the spectrometer through a 220F matching fiber adapter. The entrance and exit slits were set to $20\,\mu m$. The spectrometer was scanned between $656\text{-}657\,nm$ using a $0.01\,nm$ step size. The signal was recorded by a PMT with a stand alone high voltage

power supply (950 V) and an acquisition controller. The data was obtained in a single accumulation with a 1 second integration time.

b. Balmer line broadening recorded on microwave discharge plasmas

The width of the 656.2 nm Balmer α line emitted from microwave discharges of pure hydrogen alone, strontium or magnesium with hydrogen, and a mixture of 10% hydrogen and helium, argon, neon, krypton, or xenon was measured with a high resolution visible spectrometer. Each pure test gas or mixture was flowed through a half inch diameter quartz tube at 0.3 Torr maintained with a noble gas flow rate of 9.3 sccm or an noble gas flow rate of 8.3 sccm and a hydrogen flow rate of 1 sccm. Each gas flow was controlled by a 0-20 sccm range mass flow controller (MKS 1179A21CS1BB) with a readout (MKS type 246). The cell pressure was monitored by a 0-10 Torr MKS Baratron absolute pressure gauge. Magnesium or strontium was added to the plasma by transferring 50 mg of solid metal into the quartz tube with flowing argon. The plasma discharge partially vaporized the metal during the experiment. The tube was fitted with an Opthos coaxial microwave cavity (Evenson cavity). The microwave generator shown in Figure 3 was an Opthos model MPG-4M generator (Frequency: 2450 MHz). The input power to the plasma was set at 40 watts with forced air cooling of the cell.

The plasma emission was fiber-optically coupled through a 220F matching fiber adapter positioned 2 cm from the cell wall to a high resolution visible spectrometer with a resolution of $\pm 0.006\,nm$ over the spectral range $190\text{-}860\,nm$. The spectrometer was a Jobin Yvon Horiba 1250 M with 2400 groves/mm ion-etched holographic diffraction grating. The entrance and exit slits were set to $20\,\mu m$. The spectrometer was scanned between $655.5\text{-}657\,nm$ using a $0.005\,nm$ step size. The signal was recorded by a PMT with a stand alone high voltage power supply (950 V) and an acquisition controller. The data was obtained in a single accumulation with a 1 second integration time.

F. Electron temperature T_e measurements of microwave discharge plasmas

The most commonly used spectroscopic diagnostic method to determine the electron temperature T_e of laboratory plasmas is based on determining the relative intensities of two spectral lines as described by Griem [25]. It may be shown that for two emission lines at wavelengths λ_A and λ_B

$$\frac{I_A}{I_B} = \frac{(\sigma g_2 A_{21})_A}{(\sigma g_2 A_{21})_B} e^{-\frac{(E_{2A} - E_{2B})}{kT_e}} \tag{3}$$

where I_A and I_B are the intensities measured at λ_A and λ_B, and $\sigma \propto n^4$ for excited state atomic hydrogen. The frequency ν, the transition probability A, the degeneracy g, and the upper level E are known constants from which T_e was determined. T_e was measured on microwave plasmas of helium alone and helium-hydrogen mixture (90/10%) from the ratio of the intensity of the *He* 501.6 nm (upper quantum level $n=3$) line to that of the *He* 492.2 nm ($n=4$) line. T_e was measured on microwave plasmas of argon alone and argon-hydrogen mixture (90/10%) from the ratio of the intensity of the *Ar* 104.8 nm (upper quantum level $n=3$) line to that of the *Ar* 420.06 nm ($n=4$) line. T_e was also measured by the same method on microwave plasmas of pure hydrogen alone, strontium or magnesium with hydrogen, and a mixture of 10% hydrogen and neon, krypton, or xenon using the ratio of the intensities of two noble gas or alkaline earth metal lines in two quantum states.

The experimental set up comprising a microwave discharge gas cell light source and an UV-VIS spectrometer which was differentially pumped is shown in Figure 3. In each case, the microwave plasma cell was run under the conditions given in section B. The spectrometer was a normal incidence McPherson 0.2 meter monochromator (Model 302, Seya-Namioka type) equipped with a 1200 lines/mm holographic grating with a platinum coating. The wavelength region covered by the monochromator was $2-560\,nm$. The visible spectra ($400-560\,nm$) of the cell emission was recorded with a photomultiplier tube (PMT) and a sodium salicylate scintillator. The PMT (Model R1527P, Hamamatsu)

used has a spectral response in the range of 185 – 680 *nm* with a peak efficiency at about 400 *nm*. The scan interval was 0.4 *nm*. The inlet and outlet slit were 300 μm with a corresponding wavelength resolution of 2 *nm*. The spectra were repeated five times per experiment and were found to be reproducible within less than ±5%.

III. RESULTS AND DISCUSSION

A. EUV Spectroscopy

Extreme ultraviolet (EUV) spectroscopy was recorded on microwave and discharge cell light sources to compare Lyman α line widths from the two sources. The EUV spectra (100-170 *nm*) of emission from the discharge and microwave plasmas of argon-hydrogen mixture (97/3%) are shown in Figure 5. The microwave plasma showed significant broadening relative to the discharge plasma. The width of the microwave plasma Lyman α line was 10 *nm*; whereas, the width of the glow discharge plasma Lyman α line was 2.6 *nm*. In addition, the intensity of the Lyman α emission compared to the molecular hydrogen emission was significantly higher in the case of the microwave plasma. The Lyman α line broadening and increased intensity indicate a much higher ion temperature in the microwave plasma which was confirmed by high resolution measurements of the Balmer α line width which gave quantitative ion temperature measurements reported sections B and C. No electric field was present in the microwave plasmas. Thus, the results can not be explained by Stark broadening or acceleration of charged species due to high fields of over 10 *kV/cm* as proposed by Videnocic et al. [8] to explain excessive broadening observed in glow discharges.

B. Balmer line broadening recorded on glow discharge plasmas

The 656 nm Balmer α line width recorded with a high resolution (±0.025 *nm*) visible spectrometer on glow discharge plasmas of hydrogen compared with each of xenon-hydrogen (90/10%), strontium-hydrogen and argon-hydrogen (90/10%) are shown in Figures 6-8, respectively. The energetic hydrogen atom densities and energies of the plasmas of

hydrogen alone, strontium or magnesium with hydrogen, and hydrogen-noble gas mixtures were calculated using the method of Videnocic et al. [8] and are given in Table 1. It was found that strontium-hydrogen, helium-hydrogen, and argon-hydrogen showed significant broadening corresponding to an average hydrogen atom temperature of 23-38 eV; whereas, pure hydrogen, neon-hydrogen, krypton-hydrogen, and xenon-hydrogen showed no excessive broadening corresponding to an average hydrogen atom temperature of $\approx 4\ eV$. No voltage effect was observed with the strontium-hydrogen, helium-hydrogen, or argon-hydrogen plasmas.

C. Balmer line broadening recorded on microwave discharge plasmas

The 656 nm Balmer α line width recorded with a high resolution ($\pm 0.025\ nm$) visible spectrometer on microwave discharge plasmas of hydrogen compared with each of xenon-hydrogen (90/10%), magnesium-hydrogen, and helium-hydrogen (90/10%) are shown in Figures 9-11, respectively. The energetic hydrogen atom densities and energies of plasmas of hydrogen alone, strontium or magnesium with hydrogen, and noble gas-hydrogen mixtures were calculated using the method of Videnocic et al. [8] and are given in Table 2. It was found that the strontium-hydrogen microwave plasma showed a broadening similar to that observed in the glow discharge cell of 27-33 eV; whereas, in both sources, no broadening was observed for magnesium-hydrogen. Furthermore, the microwave helium-hydrogen, and argon-hydrogen plasmas showed extraordinary broadening corresponding to an average hydrogen atom temperature of 110-130 eV and 180-210 eV, respectively, and an atom density of $3.5\ X\ 10^{14} \pm 20\%\ atoms/cm^3$ and $4.8\ X\ 10^{14} \pm 20\%\ atoms/cm^3$, respectively. Whereas, pure hydrogen, neon-hydrogen, krypton-hydrogen, and xenon-hydrogen showed no excessive broadening corresponding to an average hydrogen atom temperature of $\approx 4\ eV$ and an atom density of only $7\ X\ 10^{13} \pm 20\%\ atoms/cm^3$ even though 10 times more hydrogen was present. These studies demonstrate excessive line broadening in the absence of an observable effect attributable to an electric field since the hydrogen emission shows no broadening.

Excessive line broadening was only observed in the cases where an ion was present which could provide a net enthalpy of reaction of an integer multiple of the potential energy of atomic hydrogen (Sr, Ar^+, or He^+). Whereas plasmas of chemically similar controls that do not provide gaseous atoms or ions that have electron ionization energies which are a multiple of $27.2\,eV$. These support the rt-plasma mechanism.

Rt-plasmas formed with hydrogen-potassium mixtures have been reported previously [17-18] wherein the plasma decayed with a two second half-life when the electric field was set to zero. This was the thermal decay time of the filament which dissociated molecular hydrogen to atomic hydrogen. This experiment showed that hydrogen line emission was occurring even though the voltage between the heater wires was set to and measured to be zero and indicated that the emission was due to a reaction of potassium atoms with atomic hydrogen. Potassium atoms ionize at an integer multiple of the potential energy of atomic hydrogen, $m \cdot 27.2\,eV$. The enthalpy of ionization of K to K^{3+} has a net enthalpy of reaction of $81.7426\,eV$, which is equivalent to $m = 3$.

A rt-plasma of hydrogen and certain alkali ions formed at low temperatures (e.g. $\approx 10^3\,K$) as recorded via EUV spectroscopy, and an excessive afterglow duration was observed by hydrogen Balmer and alkali line emissions in the visible range [18]. The observed plasma formed from atomic hydrogen generated at a tungsten filament that heated a titanium dissociator and one of potassium, rubidium, cesium, and their carbonates and nitrates. These atoms and ions ionize to provide a net enthalpy of reaction of an integer multiple of the potential energy of atomic hydrogen ($m \cdot 27.2\,eV$, $m =$ integer) to within 0.17 eV and comprise only a single ionization in the case of a potassium or rubidium ion. Whereas, the chemically similar atoms of sodium and sodium and lithium carbonates and nitrates which do not ionize with these constraints caused no emission. To test the electric dependence of the emission, the weak electric field of about 1 V/cm was set and measured to be zero in $< 0.5\,X\,10^{-6}$ sec. An afterglow duration of about one to two seconds was recorded in the case of potassium, rubidium, cesium, K_2CO_3, $RbNO_3$, and $CsNO_3$. Hydrogen line or alkali line emission was occurring even though the voltage between the heater wires was set to and measured to be zero. These atoms and ions ionize to provide a net

enthalpy of reaction of an integer multiple of the potential energy of atomic hydrogen to within less than the thermal energies at $T \approx 10^3\ K$ and comprise only a single ionization in the case of a potassium or rubidium ion. Since the thermal decay time of the filament for dissociation of molecular hydrogen to atomic hydrogen was similar to the rt-plasma afterglow duration, the emission was determined to be due to a reaction of atomic hydrogen with each of the atoms or ions that did not require the presence of an electric field to be functional.

D. T_e measurements of microwave discharge plasmas

The results of the T_e measurements on microwave plasmas of pure hydrogen alone, strontium or magnesium with hydrogen, and a mixture of 10% hydrogen and helium, neon, argon, krypton, or xenon are given in Table 2. Similarly to the ion measurement, the average electron temperature for helium-hydrogen plasma was $28{,}000 \pm 5\%\ K$; whereas, the corresponding temperature of helium alone was only $6800 \pm 5\%\ K$. The average electron temperature for argon-hydrogen plasma was $11{,}600 \pm 5\%\ K$; whereas, the corresponding temperature of argon alone was only $4800 \pm 5\%\ K$.

IV. SUMMARY AND CONCLUSIONS

The argon-hydrogen microwave plasma showed significant broadening of the width of the Lyman α line of $10\ nm$; whereas, the width of the Lyman α line emitted from the glow discharge plasma was $2.6\ nm$. In addition, the intensity of the Lyman α emission compared to the molecular hydrogen emission was significantly higher in the case of the microwave plasma. The results indicate a much greater ion temperature in the microwave plasma.

Line broadening of the hydrogen Balmer lines provides a sensitive measure of the number and energy of excited hydrogen atoms in a glow discharge plasma. The width of the 656.5 nm Balmer α line emitted from glow discharge plasmas having atomized hydrogen from pure hydrogen alone, strontium or magnesium with hydrogen, and a mixture of 10% hydrogen and helium, argon, neon, krypton, or xenon was

measured with a high resolution ($\pm 0.025\,nm$) visible spectrometer. The energetic hydrogen atom density and energies were determined from the broadening, and it was found that strontium-hydrogen, helium-hydrogen, and argon-hydrogen showed significant broadening corresponding to an average hydrogen atom temperature of $23\text{-}38\,eV$; whereas, pure hydrogen, neon-hydrogen, krypton-hydrogen, and xenon-hydrogen showed no excessive broadening corresponding to an average hydrogen atom temperature of $\approx 4\,eV$. Thus, line broadening was only observed for the ions which provided a net enthalpy of reaction of a multiple of the potential energy of the hydrogen atom.

Kuraica and Konjevic [7] and Videnocic et al. [8] studied 97% argon and 3% hydrogen mixtures in Grimm-type discharges with a hollow anode. In our studies with argon-hydrogen plasmas, the voltage was increased at 50 V increments from 275 V to 475 V, and the high resolution visible spectra were recorded to observe the effect of voltage on the Balmer α line broadening. In contrast to an increase in broadening with voltage predicted by Kuraica and Konjevic [7], no voltage effect was observed. Also, no voltage effect was also observed with the strontium-hydrogen plasma which supports the rt-plasma mechanism of the low voltage strontium-hydrogen and strontium-argon-hydrogen plasmas reported by Mills and Nansteel [14-15, 19]. Similarly, no voltage effect was observed in the case of the helium-hydrogen plasma which supports the rt-plasma mechanism as the source of the excessive broadening.

The 656.5 nm Balmer α line width measurements were repeated with microwave discharge plasmas rather than the glow discharge plasmas, and significant differences were observed between the plasma source while the same trend was observed for the particular plasma gas. It was found that the strontium-hydrogen microwave plasma showed a broadening similar to that observed in the glow discharge cell of $27\text{-}33\,eV$; whereas, in both sources, no broadening was observed for magnesium-hydrogen. Furthermore, the microwave helium-hydrogen, and argon-hydrogen plasmas showed extraordinarily higher broadening corresponding to an average hydrogen atom temperature of $110\text{-}130\,eV$ and $180\text{-}210\,eV$, respectively, and an atom density of $3.5\,X\,10^{14} \pm 20\%\ atoms/cm^3$ and $4.8\,X\,10^{14} \pm 20\%\ atoms/cm^3$, respectively.

Whereas, similarly to the glow discharge case, pure hydrogen, neon-hydrogen, krypton-hydrogen, and xenon-hydrogen showed no excessive broadening corresponding to an average hydrogen atom temperature of $\approx 4\ eV$ and an atom density of only $7 X 10^{13} \pm 20\%\ atoms/cm^3$ even though 10 times more hydrogen was present. Similarly, the average electron temperature for helium-hydrogen plasma was $28{,}000 \pm 5\%\ K$; whereas, the corresponding temperature of helium alone was only $6800 \pm 5\%\ K$. And, the average electron temperature for argon-hydrogen plasma was $11{,}600 \pm 5\%\ K$; whereas, the corresponding temperature of helium alone was only $4800 \pm 5\%\ K$.

Thus, excessive line broadening and an elevated electron temperature were only observed for the ions which provided a net enthalpy of reaction of a multiple of the potential energy of the hydrogen atom. No electric field was present in the microwave plasmas. Thus, the results can not be explained by Stark broadening or acceleration of charged species due to high fields of over $10\ kV/cm$ as proposed by Videnocic et al. [8] to explain excessive broadening observed in glow discharges. The results are consistent with an energetic reaction caused by a resonance energy transfer between hydrogen atoms and strontium atoms, Ar^+, or He^+ as the source of the excessive line broadening. The reaction rate is higher under the conditions of a microwave compared to a glow discharge plasma even at a lower input power.

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Table 1. The energetic hydrogen atom densities and energies for catalyst and noncatalyst glow discharge plasmas.

Plasma Gas	Hydrogen Atom Density[a] (10^{13} *atoms*/cm^3) (±20%)	Hydrogen Atom Energy[b] (*eV*) (±5%)
H_2	5	3-4
Mg/H_2	6	4-5
Sr/H_2	10	23-25
Ne/H_2	2.1	5-6
Kr/H_2	1	3-4
Xe/H_2	1	3-4
Ar/H_2	3	30-35
He/H_2	3	33-38

[a] Approximate Calculated [8]
[b] Calculated [8]

Table 2. The energetic hydrogen atom densities and energies and the electron temperature for catalyst and noncatalyst microwave discharge plasmas.

Plasma Gas	Hydrogen Atom Density[a] (10^{13} *atoms*/*cm*^{3}) (±20%)	Hydrogen Atom Energy[b] (*eV*) (±5%)	Electron Temperature T_e[c] (K) (±5%)
H_2	7	3-4	5500
Mg/H_2	11.1	4-5	5800
Sr/H_2	18.5	27-33	10,280
Ne/H_2	9	5-6	7800
Kr/H_2	4	3-4	6700
Xe/H_2	3	3-4	6500
Ar/H_2	35	110-130	11,600
He/H_2	48	180-210	28,000

[a] Approximate Calculated [8]
[b] Calculated [8]
[c] Calculated [25]

Figure Captions

Figure 1. Cross sectional view of the discharge cell.

Figure 2. The experimental set up comprising a discharge gas cell light source and an EUV spectrometer which was differentially pumped.

Figure 3. The experimental set up comprising a microwave discharge gas cell light source and an EUV-UV-VIS spectrometer which was differentially pumped.

Figure 4. Cylindrical stainless steel cell for studies of the broadening of the Balmer α line emitted from glow discharge plasmas of 1.) pure hydrogen alone, 2.) hydrogen with strontium or magnesium, and 3.) a mixture of 10% hydrogen and helium, argon, krypton, or xenon.

Figure 5. The EUV spectra (100-170 nm) of emission from the discharge and microwave plasmas of argon-hydrogen mixture (97/3%). The microwave plasma showed significant broadening of the width of the Lyman α line of 10 nm; whereas, the width of the Lyman α line emitted from the glow discharge plasma was 2.6 nm. In addition, the intensity of the Lyman α emission compared to the molecular hydrogen emission was significantly higher in the case of the microwave plasma. The results indicate a much greater ion temperature in the microwave plasma.

Figure 6. The 656 nm Balmer α line width recorded with a high resolution ($\pm 0.025\ nm$) visible spectrometer on a xenon-hydrogen (90/10%) and a hydrogen glow discharge plasma. No line excessive broadening was observed corresponding to an average hydrogen atom temperature of $3-4\ eV$.

Figure 7. The 656 nm Balmer α line width recorded with a high resolution ($\pm 0.025\ nm$) visible spectrometer on a strontium-hydrogen and a hydrogen glow discharge plasma. Significant broadening was observed corresponding to an average hydrogen atom temperature of $23-25\ eV$.

Figure 8. The 656 nm Balmer α line width recorded with a high resolution ($\pm 0.025\ nm$) visible spectrometer on an argon-hydrogen (90/10%) and a hydrogen glow discharge plasma. Significant broadening was observed corresponding to an average hydrogen atom temperature of $30-35\ eV$.

Figure 9. The 656 nm Balmer α line width recorded with a high resolution ($\pm 0.006\ nm$) visible spectrometer on a xenon-hydrogen

(90/10%) and a hydrogen microwave discharge plasma. No line excessive broadening was observed corresponding to an average hydrogen atom temperature of $3-4\,eV$.

Figure 10. The 656 nm Balmer α line width recorded with a high resolution ($\pm 0.006\,nm$) visible spectrometer on an magnesium-hydrogen and a hydrogen microwave discharge plasma. No line excessive broadening was observed corresponding to an average hydrogen atom temperature of $4-5\,eV$.

Figure 11. The 656 nm Balmer α line width recorded with a high resolution ($\pm 0.006\,nm$) visible spectrometer on a helium-hydrogen (90/10%) and a hydrogen microwave discharge plasma. Significant broadening was observed corresponding to an average hydrogen atom temperature of $180-210\,eV$.

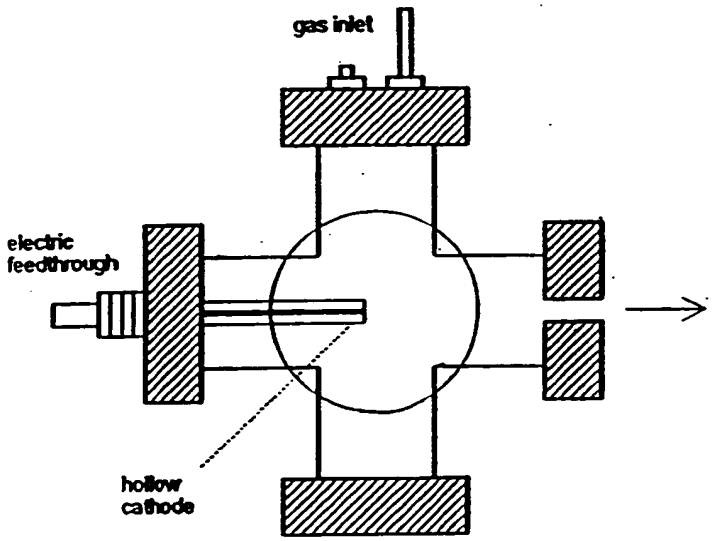
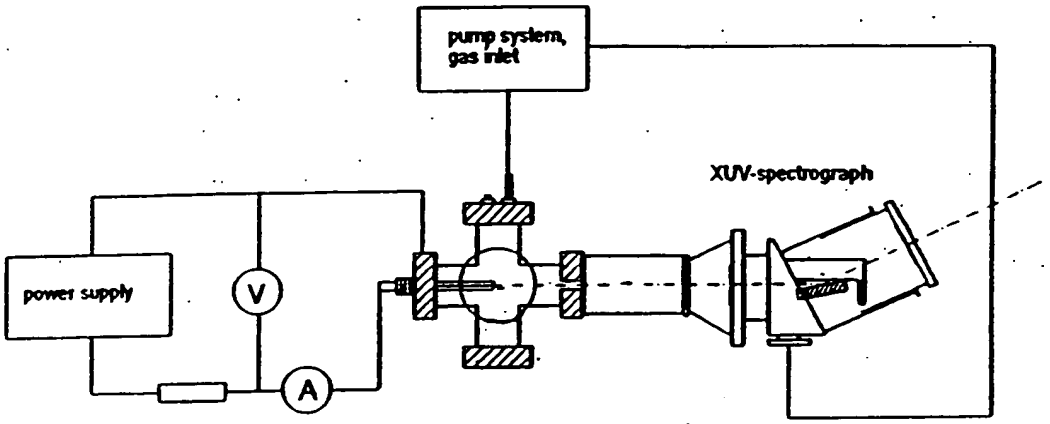


Fig. 1



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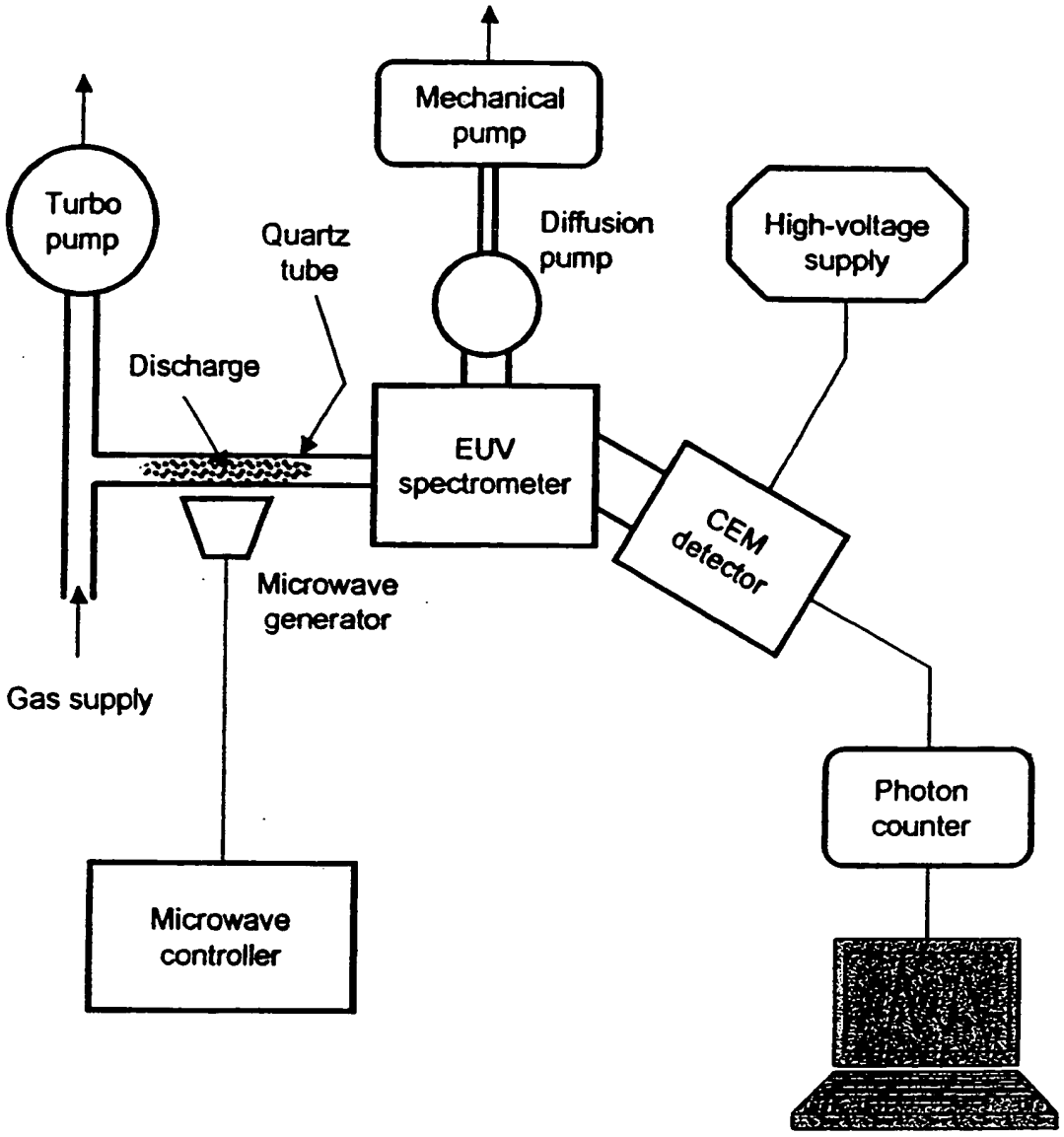
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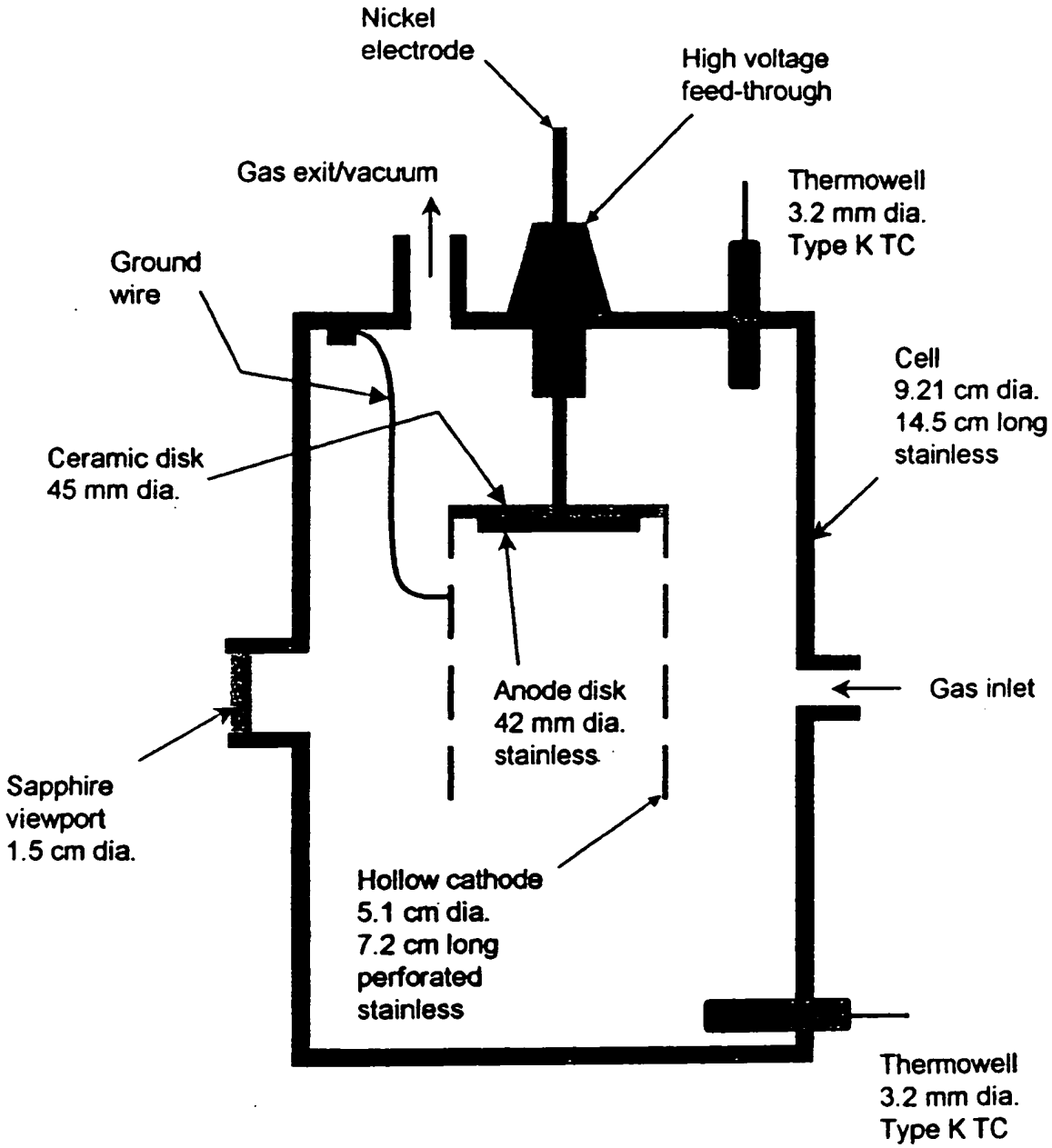
Turbo pump
Quartz tube
Diffusion pump
High-voltage supply
Discharge
EUV spectrometer
CEM detector
Microwave generator
Gas supply
Photon counter
Microwave controller

Fig. 3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High voltage feed-through
Gas exit/vacuum
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Ground wire
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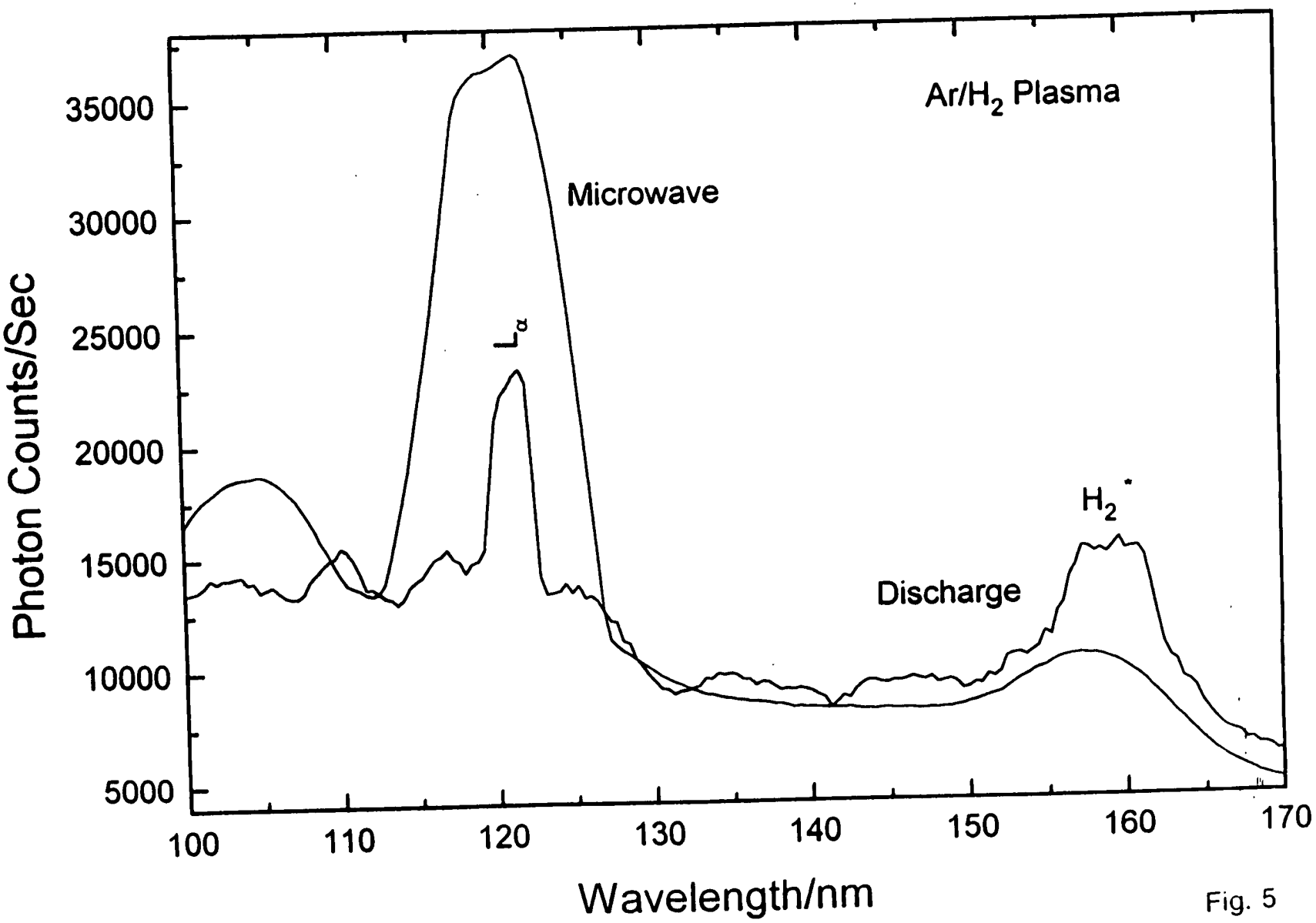
Ceramic disk 45 mm dia.
Anode disk 42 mm dia. stainless
Gas inlet
Sapphire viewport 1.5 cm dia.
Hollow cathode 5.1 cm dia. 7.2 cm long perforated stainless
Thermowell 3.2 mm dia. Type K TC

Fig. 4


Ar/H2 Plasma
Microwave
Lα
H2*
Discharge
Photon Counts/Sec
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20000
15000
10000
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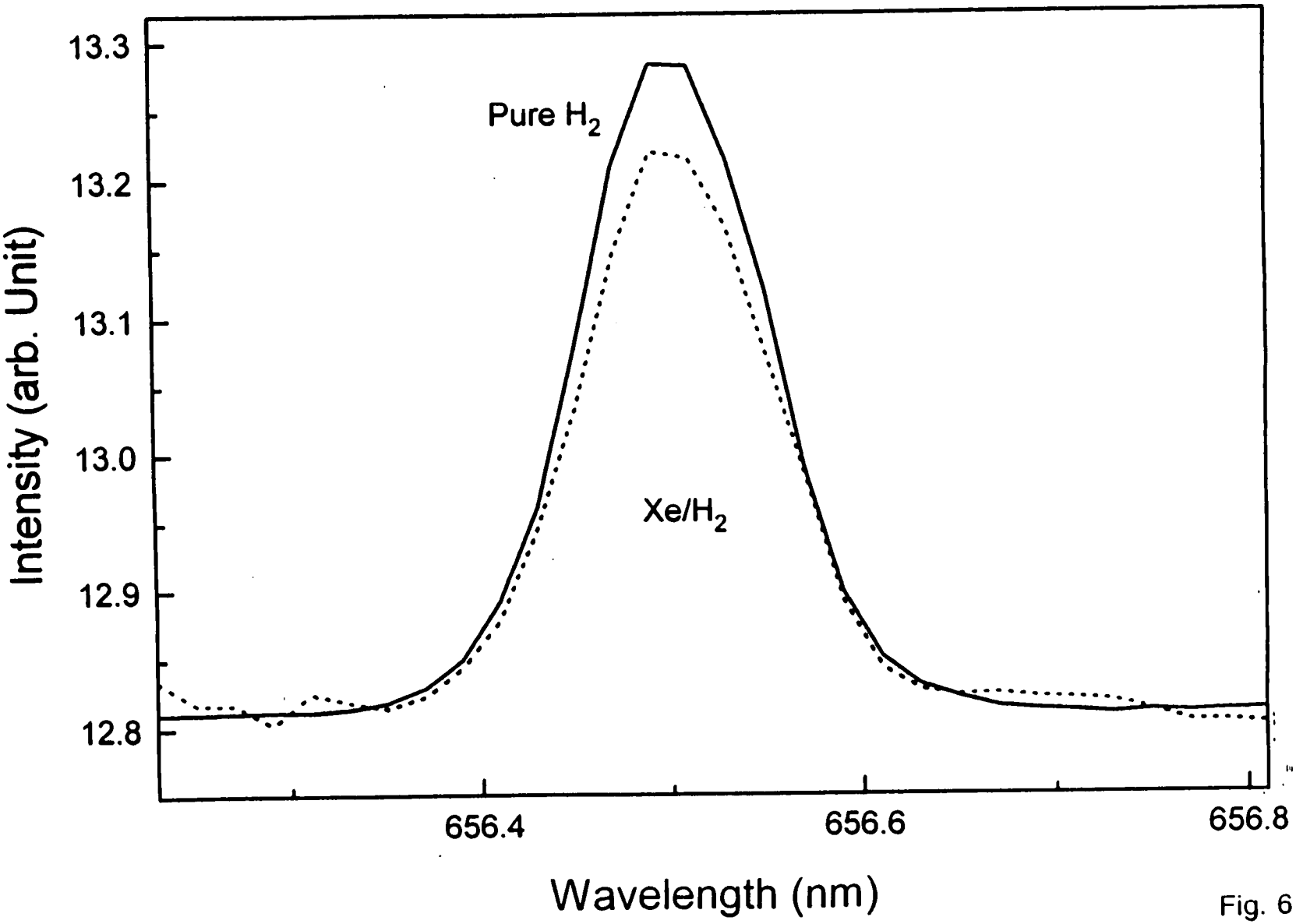
100
110
120
130
140
150
160
170
Wavelength/nm

Fig. 5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13.2
13.1
13.0
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12.8
Intensity (arb. Unit)
Pure H_2
Xe/H_2
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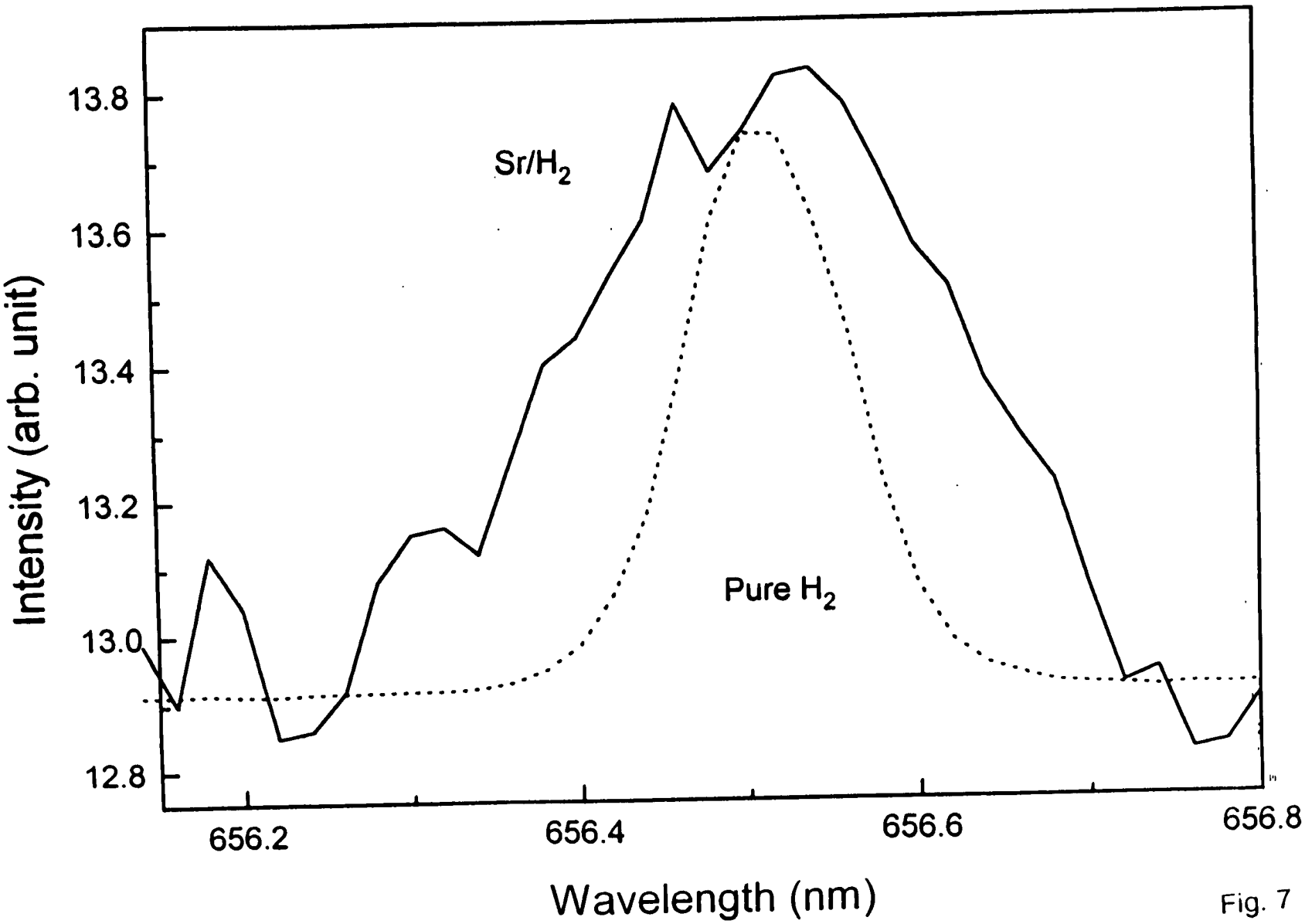
656.6
656.8
Wavelength (nm)

Fig. 6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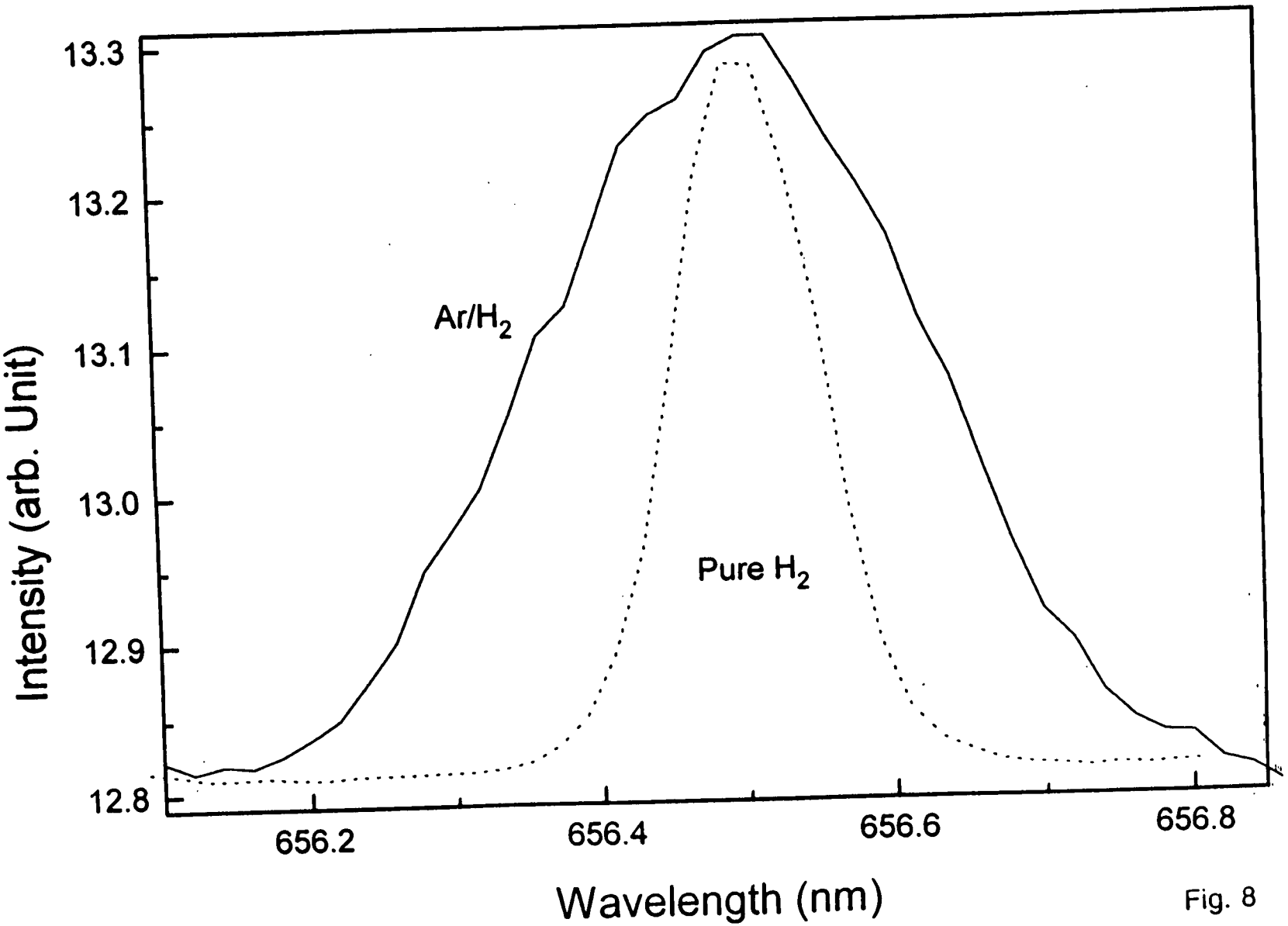
656.4
656.6
656.8
Wavelength (nm)

Fig. 7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Pure H2
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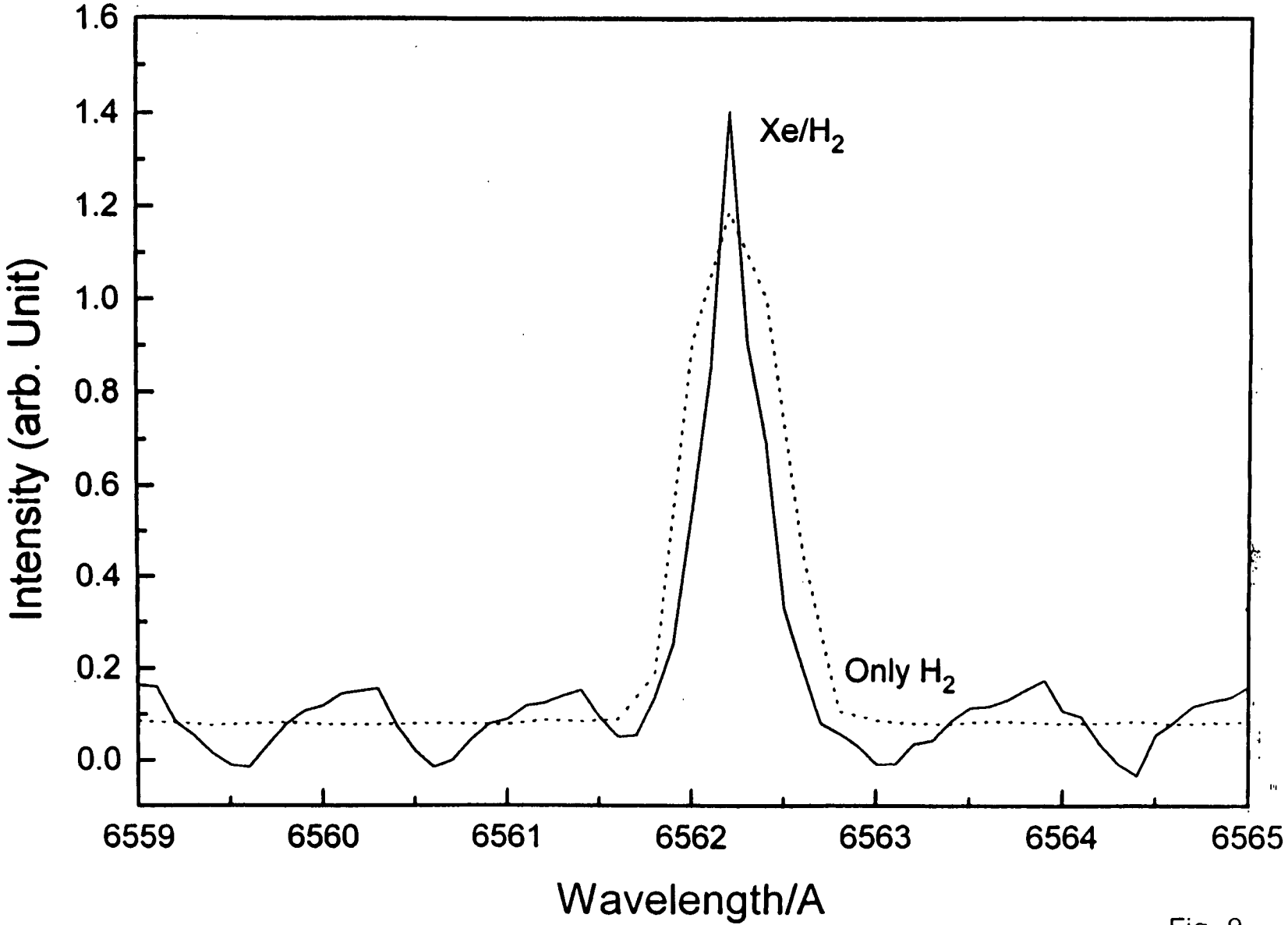
656.4
656.6
656.8
Wavelength (nm)

Fig. 8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1.4
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0.6
0.4
0.2
0.0
Intensity (arb. Unit)
Xe/H2
Only H2
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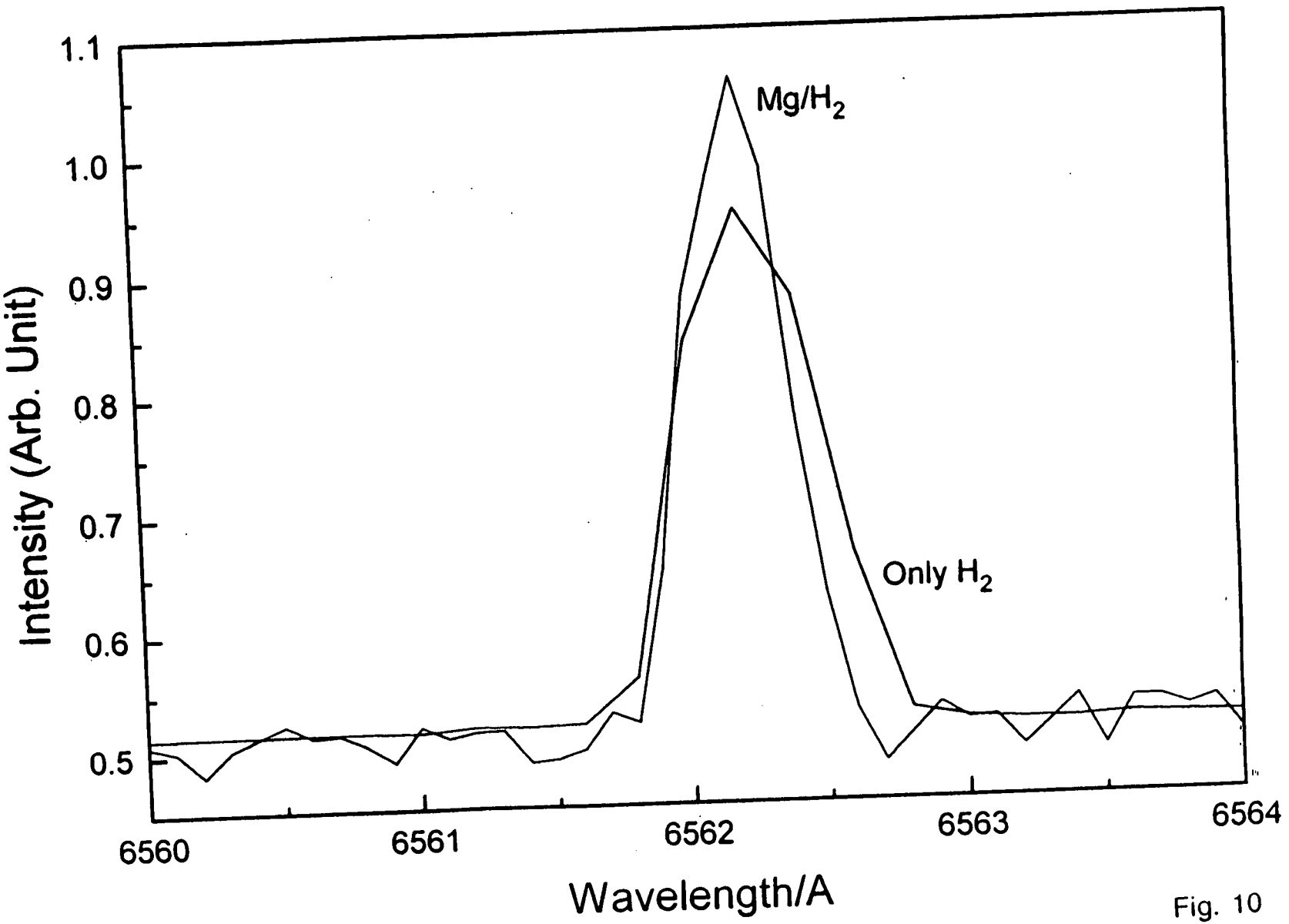
6560
6561
6562
6563
6564
6565
Wavelength/A

Fig. 9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Intensity (Arb. Unit)
Mg/H2
Only H2
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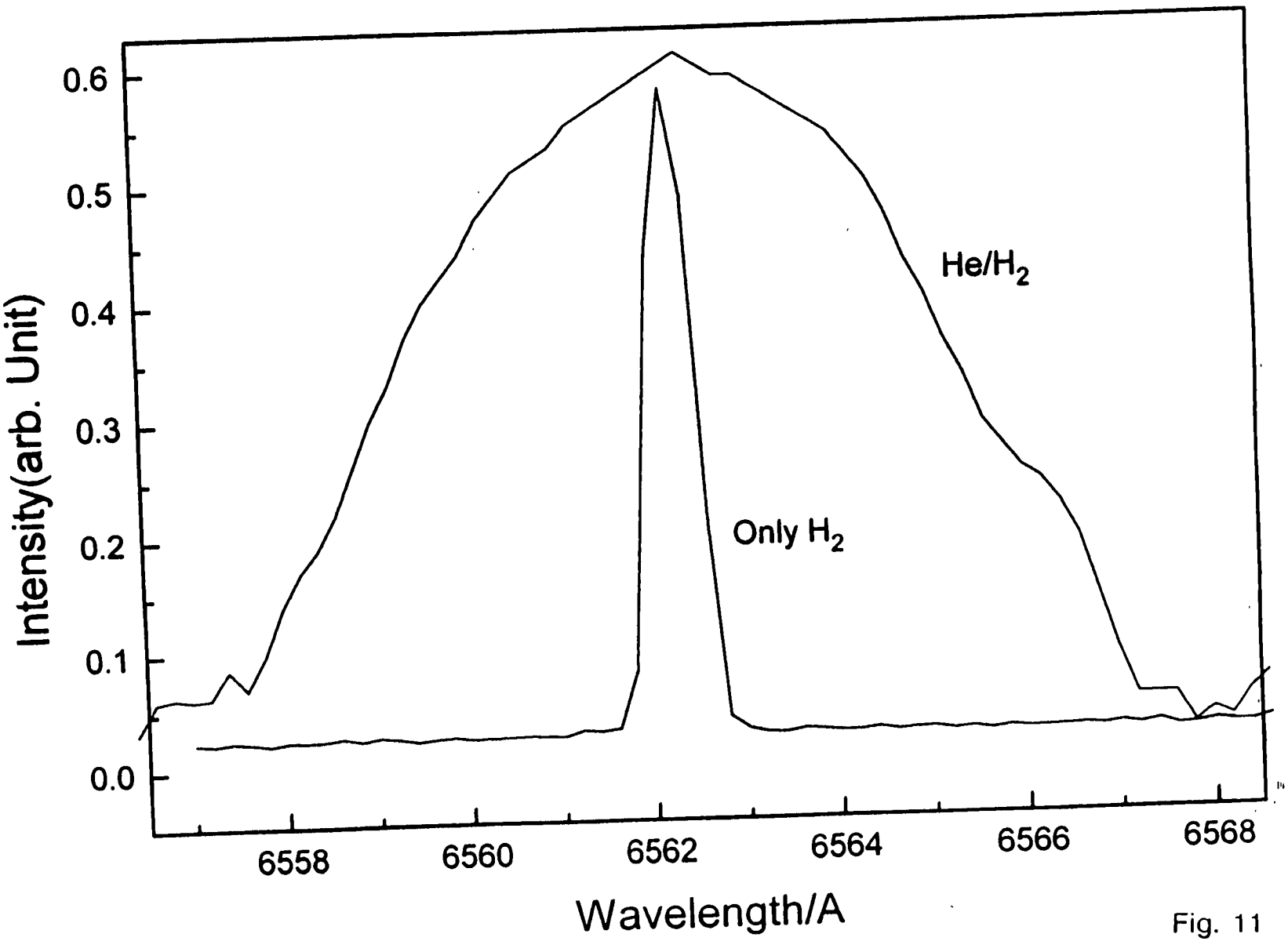
6561
6562
6563
6564
Wavelength/A

Fig. 10


Intensity(arb. Unit)
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0.6
6558
6560
6562
6564
6566
6568
Wavelength/A
He/H2
Only H2

Fig. 11